Tetrahedron Letters, Vol.22, No.37, pp 3633 - 3636, 1981
Printed in Great Britain

0040-4039/81/373633-04$02.00/0

A NOVEL CARBON-CARBON BOND FORMATION BY THE LEWIS ACID CATALYZED REACTION OF β-STYRYLSILANE WITH ACETAL

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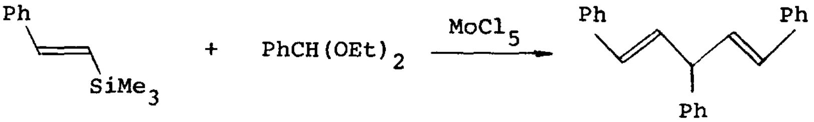
Summary: Treatment of (E)- and (Z)-β-styryltrimethylsilanes with benzaldehyde diethyl acetal in the presence of Lewis acid affords selectively 1,3,5-triphenyl-(E,E)- and (E,Z)-1,4-pentadienes, respectively.

Vinylsilanes have been known as useful synthetic intermediates, undergoing stereospecific as well as regioselective attack of electrophiles to provide a simple procedure for a novel carbon-carbon bond formation,[1] though electrophiles are limited to acid chloride[1a,b] and α-chloro ether.[1b-e] We now report the Lewis acid catalyzed reaction of β-styryltrimethylsilanes with benzaldehyde diethyl acetal to afford 1,4-pentadiene derivatives.

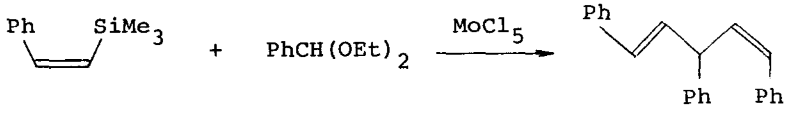
Treatment of (E)-β-styryltrimethylsilane with benzaldehyde diethyl acetal in the presence of 0.8 equiv. of MoCl$_5$ per mol of the styrylsilane gave only the 2:1 adduct, 1,3,5-triphenyl-(E,E)-1,4-pentadiene. A satisfactory result was also obtained when 0.5 equiv. of MoCl$_5$ was used. The results are shown in Table 1. A typical experimental procedure is as follows; to a suspension of MoCl$_5$ (0.187 g, 1.0 mmol) in dichloromethane (4 ml), (E)-β-styryltrimethylsilane (0.352 g, 2.0 mmol) in dichloromethane (2 ml) and then benzaldehyde diethyl acetal (0.360 g, 2.0 mmol) were added dropwise at -78°C. The mixture was stirred at -78°C for 2.5h and the reaction temperature was raised to -20°C



1a

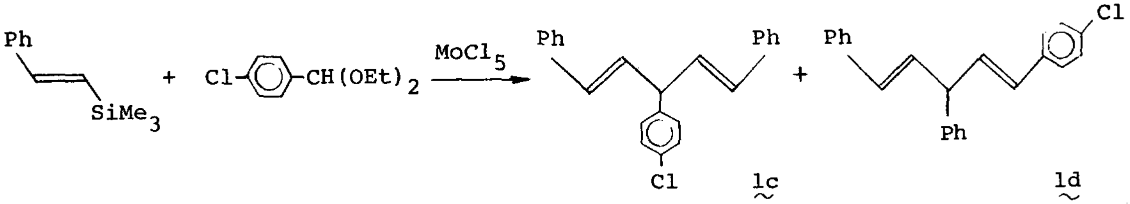
for 1.5h, followed by the addition of 1:1 mixture of methanol-water (2 ml) at -20°C. Saturated aqueous solution of sodium carbonate (2 ml) was added to the mixture, which was subsequently extracted with ether (10 ml). The extract was concentrated and chromatographed on a silica gel column eluting with benzene-hexane (1:10) to yield 1,3,5-triphenyl-(E,E)-1,4-pentadiene (1a)[2] (0.181 g, 61%). The use of WCl_6 instead of $MoCl_5$ reduced the yield of 1a. $TiCl_4$, which is a popular catalyst for the Lewis acid catalyzed reaction of allylsilane with acetal,[3] was found to be less effective than $MoCl_5$ even if the reaction was carried out at the same conditions as mentioned above. $BF_3\cdot OEt_2$ acted effectively only when reaction temperature was raised.

In the $MoCl_5$-catalyzed reaction of (Z)-β-styryltrimethylsilane with benzaldehyde diethyl acetal, 1,3,5-triphenyl-(E,Z)-1,4-pentadiene (1b)[4] was produced selectively. The selectivity was lowered when $BF_3\cdot OEt_2$ was used instead of $MoCl_5$.



1b

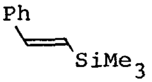
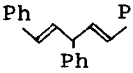
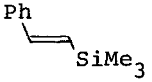
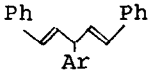
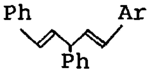
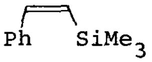
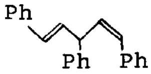
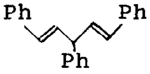
p-Chlorobenzaldehyde diethyl acetal reacted with (E)-β-styryltrimethylsilane in the presence of $MoCl_5$ to give two isomers, 1c and 1d,[5] in which the p-chlorophenyl group was substituted at the different positions.



1c 1d

The plausible reaction path is shown in Scheme 1. (E)-β-Styryltrimethylsilane undergoes the electrophilic attack of the carbonium ion 2 to form the carbonium ion 3, regioselectively, due to the stabilizing ability of the neighboring Si-C bond. The trimethylsilyl group is removed, followed by elimination of the ethoxy group by Lewis acid to give the allylic cation 4. The reaction of 4 with (E)-β-styryltrimethylsilane occurs stereospecifically to produce the (E,E)-1,4-pentadiene 1a. In the case of (Z)-β-styryltrimethylsilane, a similar addition-elimination sequence takes place to give the same

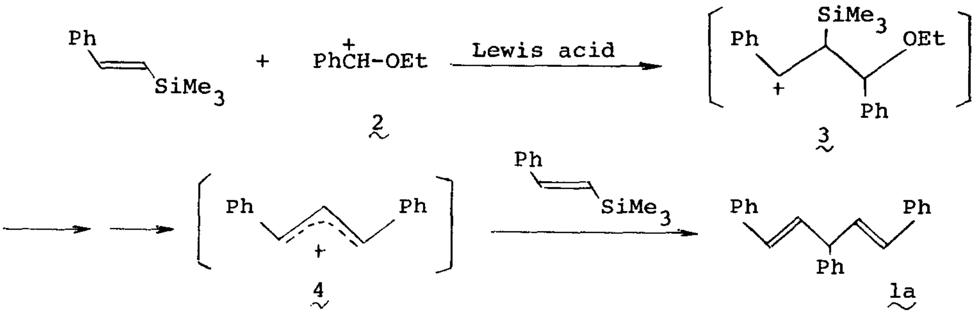
Table 1. Reaction of β-Styrylsilanes with Acetal

Styrylsilane	Acetal	Lewis acid (equiv.)		Reaction Temp.	Time	Products	Yield(%)
	PhCH(OEt)$_2$	MoCl$_5$	0.25	-78°→-20°	4h		50
			0.5				61
			0.8				62
			0.5$^{a)}$				46
		WCl$_6$	0.5	-78°→-20°	4h		34
		TiCl$_4$	1.0	-78°	4h		11
		BF$_3$·OEt$_2$	1.0	room temp.	24h		59
	ArCH(OEt)$_2$$^{b)}$	MoCl$_5$	1.0	-78°→-20°	4h	 	66
	PhCH(OEt)$_2$	MoCl$_5$	0.6	-78°→-20°	4h	 	69 (98:2)
		BF$_3$·OEt$_2$	1.0	room temp.	24h		78 (91:9)

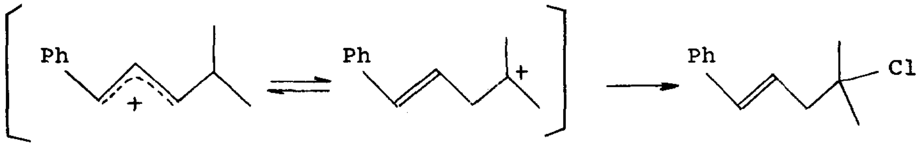
a) 0.5 equiv. of acetal per mol of β-styrylsilane was used.
b) Ar: p-Cl-C_6H_4

allylic cation 4, which is subjected to stereospecific reaction with (Z)-β-styryltrimethylsilane. The introduction of the p-chlorophenyl group in either 1 or 3 position of the 1,4-pentadiene is explained by the intervention of an unsymmetrical allylic cation.

Scheme 1



(E)-β-Styryltrimethylsilane reacted with isobutyraldehyde diethyl acetal in the presence of TiCl$_4$ in dichloromethane at room temperature for 72 h to give the 1:1 adduct, 1-phenyl-4-chloro-4-methyl-(E)-1-pentene (**1e**) in 46% yield. MoCl$_5$, however, is not effective for the present reaction. The chloride **1e** was formed by the abstraction of the chlorine atom from TiCl$_4$.



1e

Acknowledgment: This work was carried out with Grant-in-aid for Scientific Research No. 543025 from the Ministry of Education.

References and Notes

1 a) I. Fleming and A. Pearce, Chem. Commun., 633 (1975).
  b) J. P. Pillot, J. Dunogues, and R. Calas, Bull. Soc. Chim. Fr., 2143 (1975).
  c) T. H. Chan, P. W. K. Lau, and W. Mychajlowskij, Tetrahedron Lett., 3317 (1977).
  d) K. Yamamoto, O. Nunokawa, and J. Tsuji, Synthesis, 721 (1977).
  e) K. Yamamoto, J. Yoshitake, N. T. Qui, and J. Tsuji, Chem. Lett., 859 (1978).
  f) T. H. Chan and I. Fleming, Synthesis, 761 (1979).

2) **1a**: IR (neat) 1640, 955 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ4.32 (quintet, 1H, J=2.8 Hz), 6.42 (d, 4H, J=2.8 Hz), 7.08-7.33 (m, 15H); MS m/e 296 (M$^+$). Two kinds of phenyl groups were observed in the ^{13}C-NMR spectrum.

3) T. Mukaiyama, Angew. Chem., **89**, 858 (1977); Angew. Chem., Int. Ed. Engl., **16**, 817 (1977); A. Hosomi and H. Sakurai, Tetrahedron Lett., 1295 (1976).

4) **1b**: IR (neat) 1640, 1400, 965 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ4.74 (dd, 1H, J=3.2, 9.8 Hz), 5.80 (dd, 1H, J=9.8, 11.4 Hz), 6.34 (dd, 1H, J=3.2, 19.2 Hz), 6.40 (d, 1H, J=19.2 Hz), 6.56 (d, 1H, J=11.4 Hz), 7.00-7.40 (m, 15H); MS m/e 296 (M$^+$). Three kinds of phenyl groups were observed in the ^{13}C-NMR spectrum.

5) The existence of **1c** and **1d** was supported by the ^{13}C-NMR spectrum, but the ratio was not determined because it was difficult to separate each of them.

(Received in Japan 4 July 1981)